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Constant-strain-rate mechanical testing was used to study the fracture mechanical characterization of E-glass fiber fabric reinforced epoxy composites. Testing was performed as a function of the silane coupling agent used with compact tension (CT) specimens for fracture toughness and rectangular specimens for flexural strength. Two silane coupling agents, γ-aminopropyltriethoxysilane (APS) and γ-aminobutyltrithoxy-silane (ABS) were used for this purpose. The fracture toughness, K_{Ic}, of ABS treated composites was shown to be lower than that for APS treated composites. Treatment with either is better than using bare glass. A three point bend test showed the flexural strength and modulus were increased in order of untreated<ABS<APS treated composites in both dry and wet conditions. Since these silanes have similar chemistry, we believe that the difference is due to the interfacial mobility of the coupling agent layer.

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Interfacial Mobility and Its Effect on Flexural Strength and Fracture Toughness in Glass-Fiber Fabric Reinforced Epoxy Laminates

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INTRODUCTION

Composite materials are composed of two or more components that differ in physical and chemical properties which have been combined to provide specific characteristics for particular uses. The boundaries between components are typically solid interfaces. The characteristics of the interfaces are dependent on the bonding, configuration, structure, and dynamics at the interface, plus the physical and chemical properties of the constituents. As a result, the interface has a strong influence on the properties of the composite material.

The interfacial region between the components may be significantly different from the nature of the components. It is extremely difficult to make a quantitative determination of the mechanical properties of this interfacial material. Yet to improve the performance of composite materials, it is useful to clarify the properties of the interface and determine its role.

In general, inorganic materials have high surface free energies and organic materials low surface energies. For favorable combinations, when the affinity of each species for each other is low, surface treatments are often employed. Silane coupling agents are widely used as surface treatments for inorganic materials. Zisman [1] showed that the critical high surface free energy of glass treated with various silane coupling agents were changed to lower critical surface free energies, in the range near those of organic polymers.

The structure of a silane coupling agent is expressed by the general formula $(RO)_3$-Si-R', where the (RO) group represents functional groups that can be hydrolyzed to give a silanol group and R' represents groups that have affinity for, and display reactivity with, the matrix. It is widely known [2] that silane coupling agents act to increase strength and rigidity, and are particularly effective for fillers/fibers which contain silicon. Despite numerous studies, the mechanism of action of these

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agents has not yet been fully clarified. This is chiefly because the interfaces are highly complicated. This complexity probably results from various factors, such as the methods and conditions for processing the silane coupling agents, as well as the type and surface conditions of the inorganic substance.

It is possible to relate the chemical structures of the interfacial materials to the macroscopic physical or mechanical properties of composites. In many cases, the chemical reactions of interfacial species have been related to the physical properties of composites. However, fewer studies have focused on an understanding of the dynamics (i.e. molecular motion) of the system. Several spectroscopic techniques [3-4] have been applied to study these interfacial properties of the composites. In our group [5,6] we have used selectively ^{2}H-enriched coupling agents as probes for the investigation of the interfacial region by ^{2}H solid state NMR.

Previous investigations [5] using ^{29}Si CP/MAS NMR have established that the coupling agent reacts with silicon Q^2 and Q^3 sites on the surface of the silica. A comparison of two silane coupling agents, namely, γ-aminopropyltriethoxysilane(APS) and γ-aminobutyltriethoxysilane(ABS) was made using ^{2}H wide-line NMR. ABS was found to be more mobile than APS in multilayers although they have similiar chemical structures[7]. In the present study, we address the relationship between the mobility of the glass/matrix interface and the resultant flexural strength and fracture toughness by comparing composites made with the two different silane coupling agents.

EXPERIMENTAL

The heat-cleaned E-glass fiber fabrics were made by Owens-Corning Fiberglas Co. γ-aminopropyltriethoxysilane (APS) was purchased from Hüls America and used as received. γ-aminobutyltriethoxysilane (ABS) was prepared by the hydrogenation of cyanopropyltriethoxysilane (CPS) under a pressure of about 100 psi in the present of nickel catalyst [6] at 85 °C.

A 2% silane coupling agent was hydrolyzed in acetone /distilled water (10/1) for 24 hours, along with the glass fabrics which were cut into 6 by 6 square inch pieces immersed into the solution for 24 hrs at room temperature. The treated glass fabrics were washed several times with distilled water and then dried in

a vacuum oven at 110 °C for half an hour.

Epoxy resin and hardener were obtained from the Dow Chemical Company and labelled as DER331 and DEH20, respectively. A 10:1 epoxy/hardener was well mixed by stirring for several minutes. Laminates were obtained by hand lay-up with 16-24 treated or untreated glass fabric layers in a 6"x 6" aluminum mold. They were cured in a hot press by compression molding at 115 °C for 30 minutes with a pressure about 1000 psi. A postcure at 140 °C for one hour was applied subsequently to to completely cure it.

The 6" by 6" hot pressed, in-situ composites were cut into 3" long and 1" wide specimens using a band saw. These were tested for flexural strength and modulus based on ASTM standard 0790-86 [8]. The testing was done on Instron model 4204 with a loading rate of 1.27 mm/min. At least, six specimens from each sample plate were used. The flexural strength, S, was calculated from the force at break, P, from:

$$S = (3PL/2bd^2) \tag{1}$$

where L is the span between two support beams, b is width, and d is depth of the specimen. The flexural modulus, E, was calculated from:

$$E = (mL^3/4bd^3) \tag{2}$$

where the m is the slope of the stress-strain curve.

The geometry of a compact tension (CT) specimen is shown in Fig. 1. The specimens were formed into ASTM-E 399-83 [9] specimens with thickness about 0.1" and the precracks were cut with a diamond saw. The crosshead loading rate of the Instron was 0.025 in/min. The fracture toughness, K_c, was calculated by:

$$K_c = (P_c/BW^{1/2}) f(a/w) \tag{3}$$

where P_c is maximum load in a loading cycle and f(a/w) is the finite width correction. The finite width correction and other structural variables, are shown in Figure 1. The critical energy release rate, G_c is proportional to the stress intensity factor, K_c, using the relationship:

$$G_c = K_c^2/E \tag{4}$$

where E is the modulus of the composites.

RESULTS AND DISCUSSION

The flexural strength, modulus and maximum strain at break for all the composites are shown in Table I. The untreated

composite, cured at 115 °C for 30 min, but without postcure has the lowest value of flexural strength and modulus. This was obviously due to the incomplete curing which results in more void volume and lower network density. The strength and modulus of the postcured composite was higher. Silane coupling agent treated composites are measurably stronger and stiffer than those of the untreated specimens although we note that that relatively uncertainty in the modulus measurements is large. Fiber treatment results in a bridge being built-up by the coupling agents which connects the fiber and resin. ABS treated specimens have lower flexural strength and modulus than APS treated ones. We believe that this is probably due to the longer chain length of ABS and its concomitant higher mobility. A similar trend was found for the maximum strain at break. This was found to increase in order of untreated<ABS<APS treated composites.

The flexural strength and modulus of all specimens measured dry are much higher than those measured wet. It is noteworthy that the flexural modulus of the ABS treated specimens are much closer to untreated composites when dry, but are relatively better when tested wet. This suggests that even though a particular silane coupling agent was not especially effective in the dry state, it may still reduce the effect of the moisture in certain cases.

The effect of silane coupling agents on K_c and G_c values measured by a compact tension test on the glass fiber fabric reinforced epoxy composites. K_c and G_c values increased in order of untreated<ABS<APS treated composites.

CONCLUSIONS

Constant strain-rate mechanical tests, provide a technique by which surface finishes on the glass fabrics reinforced epoxy composites can be evaluated. Flexural strength, modulus, and also fracture toughness are influenced by the type of the silane coupling agent used. Untreated composites had the lowest flexural strength and modulus resulting from the poor interface between fiber fabrics and resin.

The APS treated composite has the highest flexural strength and modulus. This means that the coupling agent layer can effectively transfer the load between fiber and resin. The ABS treated composites behave in a manner that is between the

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untreated and APS-treated composites. The lower strength and modulus obtained for ABS-treated, compared to the APS-treated composite suggests a weaker interface. It is interesting that the flexural modulus of the ABS treated composites was very close to the untreated composites while tested under dry conditions, but it was relatively better when tested in wet conditions. Both stress intensity factors and critical energy release rate were increased in the order of untreated<ABS-<APS-treated composites. We believe that this is probably due to the shorter alkyl chain length of the APS which results in a less mobile material than ABS at the coupling agent/epoxy interface. This provides a better graded interface than when ABS is used.

ACKNOWLEDGMENT

REFERENCES

1. Zisman, W. A. 'Surface Chemistry of Plastics Reinforced by Strong Fibers', Ind. Eng. Chem. Prod. Res. Dec. 1969, 8, 98.
2. Plueddemann, E. P. 'Silane Coupling Agents', 2nd ed., Plenum   Press, New York, 1991.
3. Ishida, H. and Kumareds, G. 'Molecular Characterization of Composite Interfaces', Plenum Press, New York, 1985, p25.
4. Ishida, H. and Koeing, J. L. J. Colloid Interface Sci., 1978, 64, 555.
5. Kang, H. J. and Blum, F. D. Macromolecules, 1992, 25, 4526.
6. Kang, H. J., Meesiri, W. and Blum, F. D. Mater. Sci Eng. 1990, A126, 265.
7. Blum, F. D., Meesiri, W., Kang, H. J. and Gambogi, J. E. J. Adhesion Sci. Technol. 1991, 5, 479.
8. Standard Test Methods for Flexural Properties of Plastics and Electrical Insulating Materials; Lukens, R. P.; Ed.; Annual Book of ASTM Standards; American Society for Testing and Materials: Pennsylvania, 1972, part 35, p1.
9. Standard Test Methods for Plain-Strain Fracture Toughness of Metallic Materials, 1984 Annual Book of ASTM Standards, Vol. 03.01, pp.519-554: Pennsylvania.

B=0.5W
H=0.6W
W1=1.25W
F=2E=0.55W
D=0.25W
a=0.45-0.55W
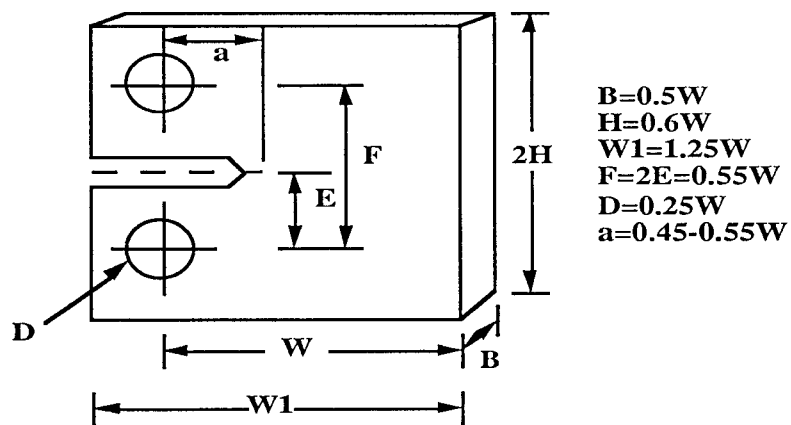
$$K_I = \frac{LOAD}{BW^{1/2}} \cdot f\left(\frac{a}{w}\right)$$

$$f\left(\frac{a}{w}\right) = \frac{(2+a/w)[.886+4.64(a/w)-13.32(a/w)^2+1.72(a/w)^3-5.6(a/w)^4]}{(1-a/w)^{3/2}}$$

Figure 1. ASTM-E399-83 Compact Tension (CT) Specimen

Table I. Three-point-bending test results for treated and untreated composites.

(a)Flexural Strength (MPa)	Dry	Wet
Untreated(w/o postcure)	372 ± 5	254 ± 25
Untreated(w/c postcure)	449 ± 40	389 ± 23
ABS treated	510 ± 19	459 ± 7
APS treated	566 ± 9	510 ± 54

(b)Flexural Modulus (MPa)	Dry	Wet
Untreated(w/o postcure)	27 ± 1.0	18.2 ± 2.5
Untreated(w/c postcure)	28 ± 0.5	23.6 ± 1.0
ABS treated	28 ± 1.0	26.0 ± 1.4
APS treated	29 ± 1.4	28.4 ± 1.7

(c)Maximum Strain at Break (in)	Dry	Wet
Untreated(w/c postcure)	0.145 ± 0.001	0.143 ± 0.006
ABS treated	0.154 ± 0.011	0.147 ± 0.003
APS treated	0.175 ± 0.004	0.156 ± 0.017

Table II. Mode 1 fracture toughness results of treated and untreated composites.

	Stress Intensity Factor k_{1c}(MN/m$^{3/2}$)	Critical Energy Release Rate G_{1c}(KJ/m^2)
Untreated	17.11 ± 0.21	10.48 ± 0.45
ABS treated	19.93 ± 1.02	14.33 ± 2.11
APS treated	22.28 ± 0.92	17.13 ± 2.38